

#12/C
v13
6/7/12

Clean Version of New Claims: #1-45

This set of claims replaces all previous claims submitted with the
March 14, 2000 (initial application)

The Old Claims #1-45 of original application are cancelled

Application number: #09/525,176

Filing Date: 03/14/2001

Inventors: Dr. Savvas Vasileiadis,

Dr. Zoe Ziaka

Zivatech Institute

89 1. (new) A process for conducting catalytic steam and carbon dioxide hydrocarbon reforming, steam alcohol reforming, water gas shift, and dehydrogenation reactions of paraffins, for the production and use of pure hydrogen which includes:

(needs process maps)

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next inner and a most inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the most inner permeable cylinder to be filled with catalyst and include gas heating tubes located along the inner axis, with the catalyst in pellet or particle form to be a reforming, water gas shift or dehydrogenation catalyst, with hydrogen to be continuously removed via permeation along the most inner membrane wherein the membrane is made by an inorganic or composite material, with the remaining reaction species to partially permeate as well via the most inner membrane, and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only to be continuously removed via permeation along the next inner membrane in order to allow for continuous hydrogen withdrawal out of the most inner catalytic zone and for continuous equilibrium shift of the reactions evolving within this zone, with the next inner membrane to be made by a metal or non-porous inorganic material permeable only to hydrogen, with the permeated pure hydrogen in the far outer cylindrical zone to be consumed in consecutive hydrogenation reactions or as fuel in consecutive gas turbines, gas engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide, and phosphoric acid types, and with the emitted hot flue gas from the fuel

cells, turbines and engines to be used for at least partial heating of most inner catalytic zone by flowing it via the location of most inner gas heating tubes.

90

2. (new) The process of claim 1, wherein a sweep reactive component is flowing via the far outer cylindrical space and reacts with the hydrogen permeated via the next inner membrane on a catalyst bed located within far outer cylinder, with the flowing reactive component to be selected from the group consisting of

an unsaturated hydrocarbon such as ethylene, acetylene, propylene, butylene for hydrogenation into ethane, ethylene, propane, butane respectively,

carbon monoxide for hydrogenation into methanol or gasoline range hydrocarbons,

nitrogen for hydrogenation into ammonia,

a higher paraffin such as hexane for hydrocracking into a mixture of paraffins and olefins with lower carbon atoms, such as butane, propane, propylene and ethylene,

an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to the corresponding saturated component,

an aldehyde or ketone for reduction with hydrogen to the corresponding alcohol such as methanol, ethanol, propanol, butanol,

an alkyl or aryl halide for reduction with hydrogen to the corresponding non-halogen component via hydrogenolysis,

a nitroalkane or aromatic nitro compound for reduction with hydrogen to the corresponding primary amine.

91

3. (new) The process of claim 1 wherein the inorganic or composite membrane of most inner permeable cylinder is rendered catalytic with the metal catalyst selected from the group consisting of nickel (Ni), chromium (Cr), ruthenium (Ru), rhodium (Rh), platinum (Pt), palladium (Pd), copper (Cu), zinc (Zn), cobalt (Co).

92

4. (new) A process for conducting catalytic steam and carbon dioxide hydrocarbon reforming, steam-alcohol reforming, water gas shift, and dehydrogenation reactions of paraffins, for production and use of pure hydrogen which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders to be filled with catalyst, with the catalyst in pellet or particle form to be a reforming, water gas shift, or dehydrogenation catalyst, with hydrogen to be continuously removed via permeation along the next-inner membrane wherein the membrane is made by an inorganic or composite material, with the remaining reaction species to partially permeate as well via the next inner membrane, and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only to be continuously removed via permeation along the most inner membrane in order to allow for continuous

hydrogen withdrawal out of the far outer catalytic zone and for continuous equilibrium shift of the reactions evolving within this zone, with the most inner membrane to be made by a metal or non-porous inorganic material permeable only to hydrogen, with the permeated pure hydrogen in the most inner cylindrical zone to be consumed in consecutive hydrogenation reactions or as fuel in consecutive gas turbines, gas engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide, and phosphoric acid types, and with the emitted hot flue gas from the fuel cells, turbines, and engines to be used for at least partial heating of the far outer catalytic zone by flowing it via the external surface of the far outer impermeable cylinder.

93
5. (new) The process of claim 4, wherein a sweep reactive component is flowing via the most inner cylindrical space and reacts with the hydrogen permeated via the most inner membrane on a catalyst bed located within most inner cylinder, with the flowing reactive component to be selected from the group consisting of

an unsaturated hydrocarbon such as ethylene, acetylene, propylene, butylene for hydrogenation into ethane, ethylene, propane, butane respectively,

carbon monoxide for hydrogenation into methanol or gasoline range hydrocarbons,

nitrogen for hydrogenation into ammonia,

a higher paraffin such as hexane for hydrocracking into a mixture of paraffins and olefins with lower carbon atoms, such as butane, propane, propylene and ethylene,

an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to the corresponding saturated component,

an aldehyde or ketone for reduction with hydrogen to the corresponding alcohol such as methanol, ethanol, propanol, butanol,

an alkyl or aryl halide for reduction with hydrogen to the corresponding non-halogen component via hydrogenolysis,

a nitroalkane or aromatic nitro compound for reduction with hydrogen to the corresponding primary amine.

94
6. (new) The process of claim 4 wherein the inorganic or composite membrane of next inner permeable cylinder is rendered catalytic with the metal catalyst selected from the group consisting of nickel (Ni), chromium (Cr), ruthenium (Ru), rhodium (Rh), platinum (Pt), palladium (Pd), copper (Cu), zinc (Zn), cobalt (Co).

95
7. (new) The process of claim 1, as applies to the steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols and water gas shift reactions, with the reject exit stream from the most inner and next inner annular zones to remove the contained steam by condensation, and subsequently be passed through a membrane permeator wherein the contained in stream hydrogen and carbon dioxide are separated by permeation via a membrane made by a polymer, inorganic, or composite material, and the non permeated hydrocarbons, alcohols, and carbon monoxide exit from the non-permeate side of the permeator as a reject stream, with the separated hydrogen and

carbon dioxide product mixture to be used for methanol synthesis and as a combined fuel-oxidant feed in a molten carbonate fuel cell.

94

8. (new) The process of claim 4, as applies to the steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, and water gas shift reactions, with the reject exit stream from the far outer and next inner annular zones to remove the contained steam by condensation, and subsequently be passed through a membrane permeator wherein the contained in stream hydrogen and carbon dioxide are separated by permeation via a membrane made by organic polymer, or inorganic, or composite material, and the non permeated hydrocarbons, alcohols, and carbon monoxide exit from the non-permeate side of the permeator as a reject stream, with the separated hydrogen and carbon dioxide product mixture to be used for methanol synthesis and as a combined fuel-oxidant feed in a molten carbonate fuel cell.

97

9. (new) The process of claim 7, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is fed in a consecutive steam reforming reactor for additional production of hydrogen and carbon dioxide gases.

98

10. (new) The process of claim 8, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is fed in a consecutive steam reforming reactor for additional production of hydrogen and carbon dioxide gases.

99

11. (new) The process of claim 7, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is recycled into the initial catalytic most inner reforming zone for continuous reforming reactions.

100

12. (new) The process of claim 8, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is recycled into the initial catalytic far outer reforming zone for continuous reforming reactions.

101

13. (new) The process of claim 1, as applies to the steam and carbon dioxide reforming of hydrocarbons, wherein the reject gas stream from most inner and next inner annular zones is fed in a consecutive impermeable catalytic tubular reactor wherein continuous steam and carbon dioxide reforming reactions of the unreacted hydrocarbons take place, with the product hydrogen and carbon monoxide gas mixture from the consecutive reforming reactions to exit from the single reactor outlet and used in consecutive chemical synthesis reactions or as fuel gas in consecutive gas turbines, gas engines, and fuel cells of molten carbonate and solid oxide types.

102

14. (new) The process of claim 4, as applies to the steam and carbon dioxide reforming of hydrocarbons, wherein the reject gas stream from the far outer and next inner annular zones is fed in a consecutive impermeable catalytic tubular reactor wherein continuous steam and carbon dioxide reforming reactions of the unreacted hydrocarbons

take place, with the product hydrogen and carbon monoxide gas mixture from the consecutive reforming reactions to exit from the single reactor outlet and used in consecutive chemical synthesis reactions or as fuel gas in consecutive gas turbines, gas engines, and fuel cells of molten carbonate and solid oxide types.

103
15. (new) The process of claim 1 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas rich in methane, landfill gas rich in methane, flue gas rich in methane, biomass gas rich in methane.

104
16. (new) The process of claim 1 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas rich in CH_4 and CO_2 , coal gas rich in CH_4 and CO_2 , landfill gas rich in CH_4 and CO_2 , biomass gas rich in CH_4 and CO_2 , other primary, secondary, refinery, and flue gas mixtures rich in CH_4 and CO_2 .

105
17. (new) The process of claim 4 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas rich in methane, landfill gas rich in methane, flue gas rich in methane, biomass gas rich in methane.

106
18. (new) The process of claim 4 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH₄ and CO₂ mixture, acidic natural gas rich in CH₄ and CO₂, coal gas rich in CH₄ and CO₂, landfill gas rich in CH₄ and CO₂, biomass gas rich in CH₄ and CO₂, other primary, secondary, refinery, and flue gas mixtures rich in CH₄ and CO₂.

107
19. (new) The process of claim 1, as applies to the dehydrogenation reaction of paraffins wherein the reject gas stream from the most inner and next inner annular zones which is rich in product olefins is fed in a consecutive polymerization reactor for production of polyolefins, or in a consecutive synthesis reactor for production of specialty chemicals.

108
20. (new) The process of claim 4, as applies to the dehydrogenation reaction of paraffins wherein the reject gas stream from the far outer and next inner annular zones which is rich in product olefins is fed in a consecutive polymerization reactor for production of polyolefins, or in a consecutive synthesis reactor for production of specialty chemicals.

109
21. (new) The process of claim 19, wherein the feed stream for the occurring dehydrogenation reaction consists of either ethane, propane, or ethane-propane mixture and the final product in the consecutive polymerization reaction is either polyethylene polymer, polypropylene polymer, or polyethylene-polypropylene copolymer.

110
22.

(new) The process of claim 20, wherein the feed stream for the occurring dehydrogenation reaction consists of either ethane, propane, or ethane-propane mixture and the final product in the consecutive polymerization reaction is either polyethylene polymer, polypropylene polymer, or polyethylene-polypropylene copolymer.

111
23.

(new) The process of claim 19, wherein the feed stream for the occurring dehydrogenation reaction consists of ethane and the final product from the consecutive chemical synthesis reaction is one of the following species ethylene oxide, ethylene glycol, acetaldehyde, acrolein, acrylic acid.

112
24.

(new) The process of claim 19, wherein the feed stream for the occurring dehydrogenation reaction consists of propane and the final product from the consecutive chemical synthesis reaction is one of the following species acrylonitrile, propylene oxide, propylene glycol.

113
25.

(new) The process of claim 20, wherein the feed stream for the occurring dehydrogenation reaction consists of ethane and the final product from the consecutive chemical synthesis reaction is one of the following species ethylene oxide, ethylene glycol, acetaldehyde, acrolein, acrylic acid.

114
26.

(new) The process of claim 20, wherein the feed stream for the occurring dehydrogenation reaction consists of propane and the final product from the consecutive

chemical synthesis reaction is one of the following species acrylonitrile, propylene oxide, propylene glycol.

1115
27. (new) The process of claim 19, wherein the feed stream for the occurring dehydrogenation reaction consists of isobutane and the final product from the consecutive chemical synthesis reaction is methyl tert-butyl ether.

C1
1116
28. (new) The process of claim 20, wherein the feed stream for the occurring dehydrogenation reaction consists of isobutene and the final product from the consecutive chemical synthesis reaction is methyl tert-butyl ether.

1117
29. (new) The process of claim 1, as applies to the steam and carbon dioxide reforming of hydrocarbons, with the reject exit stream from the most inner and next inner annular zones to remove the contained steam by condensation and subsequently be passed through a cryogenic separator wherein the contained in stream hydrogen and carbon monoxide are separated as gases while the hydrocarbons and carbon dioxide are separated as condensed liquids and after heating are recycled back into the inlet of the preceding catalytic reforming zone, with the separated hydrogen and carbon monoxide product mixture coming from the cryogenic separator to be used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines, for synthesis gas of methanol and gasoline range hydrocarbons.

5/1/8
30.

(new) The process of claim 4, as applies to the steam and carbon dioxide reforming of hydrocarbons, with the reject exit stream from the far outer and next inner annular zones to remove the contained steam by condensation and subsequently be passed through a cryogenic separator wherein the contained in stream hydrogen and carbon monoxide are separated as gases while the hydrocarbons and carbon dioxide are separated as condensed liquids and after heating are recycled back into the inlet of the preceding catalytic reforming zone, with the separated hydrogen and carbon monoxide product mixture coming from the cryogenic separator to be used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines, for synthesis gas of methanol and gasoline range hydrocarbons.

5/1/9
31.

(new) The process of claim 29, wherein the separated liquefied hydrocarbons and carbon dioxide components from the cryogenic separator are mixed with steam and fed into a consecutive carbon dioxide and steam hydrocarbon reforming reactor for additional production of hydrogen and carbon monoxide which is used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines, for synthesis gas of methanol and gasoline range hydrocarbons.

5/1/9
32.

(new) The process of claim 30, wherein the separated liquefied hydrocarbons and carbon dioxide components from the cryogenic separator are mixed with steam and fed into a consecutive carbon dioxide and steam hydrocarbon reforming reactor for

additional production of hydrogen and carbon monoxide which is used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines, for synthesis gas of methanol and gasoline range hydrocarbons.

33. (new) The process of claim 1 as applies to the steam and carbon dioxide reforming of hydrocarbons, including methane as a hydrocarbon, wherein the reject exit stream consists of hydrogen, carbon monoxide, and unreacted steam which enters as a fuel gas feed into a solid oxide fuel cell or into a molten carbonate fuel cell for continuous generation of electricity, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well in the fuel cell inlet in order to provide for additional hydrogen fuel.

34. (new) The process of claim 4 as applies to the steam and carbon dioxide reforming of hydrocarbons, including methane as a hydrocarbon, wherein the reject exit stream consists of hydrogen, carbon monoxide, and unreacted steam which enters as a fuel gas feed into a solid oxide fuel cell or into a molten carbonate fuel cell for continuous generation of electricity, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well in the fuel cell inlet in order to provide for additional hydrogen fuel.

35. (new) The process of claim 1 as applies to the carbon dioxide and steam reforming of hydrocarbons, wherein the reject exit stream consists of hydrogen, carbon

monoxide, carbon dioxide and unreacted steam, which after the removal of steam by condensation, enters in a consecutive methanol synthesis reactor for catalytic production of methanol, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well into the methanol reactor inlet in order to provide for additional hydrogen for the reaction.

CI
1/24
36. (new) The process of claim 4 as applies to the carbon dioxide and steam reforming of hydrocarbons, wherein the reject exit stream consists of hydrogen, carbon monoxide, carbon dioxide and unreacted steam, which after the removal of steam by condensation, enters in a consecutive methanol synthesis reactor for catalytic production of methanol, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well into the methanol reactor inlet in order to provide for additional hydrogen for the reaction.

1/25
37. (new) The process of claim 35 wherein part or all of the methanol produced in the consecutive synthesis reactor is used as feed in a methanol driven fuel cell for electricity generation.

1/26
38. (new) The process of claim 36 wherein part or all of the methanol produced in the consecutive synthesis reactor is used as feed in a methanol driven fuel cell for electricity generation.

127
39. (new) The process of claim 1 as applies to the carbon dioxide and steam reforming of hydrocarbons, wherein the reject exit stream consists of hydrogen, carbon monoxide, carbon dioxide and unreacted steam, which after the removal of steam by condensation, is used for production of gasoline range hydrocarbons in a consecutive catalytic reactor with part or all of the permeate hydrogen coming out of the preceding membrane zone to be used as feed into the hydrocarbon synthesis reactor to provide for additional hydrogen for the reaction.

C 128
40. (new) The process of claim 4 as applies to the carbon dioxide and steam reforming of hydrocarbons, wherein the reject exit stream consists of hydrogen, carbon monoxide, carbon dioxide and unreacted steam, which after the removal of steam by condensation, is used for production of gasoline range hydrocarbons in a consecutive catalytic reactor with part or all of the permeate hydrogen coming out of the preceding membrane zone to be used as feed into the hydrocarbon synthesis reactor to provide for additional hydrogen for the reaction.

129
41. (new) A process for conducting catalytic carbon dioxide hydrocarbon reforming, and dehydrogenation reactions of paraffins, for production and use of pure hydrogen and carbon dioxide which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane,

C1
with the annular space between the far outer and next-inner cylinders to be filled with catalyst, with the catalyst in pellet or particle form to be a reforming or dehydrogenation catalyst, with hydrogen and carbon dioxide to be continuously removed via permeation along the next-inner membrane wherein the membrane is made by an inorganic or composite material, with the remaining reaction species to partially permeate as well via the next inner membrane and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen and carbon dioxide species to be continuously removed via permeation along the most inner membrane, with the most inner membrane to be made by an inorganic, polymer, or composite material which is permeable to both hydrogen and carbon dioxide species, with the permeated binary hydrogen-carbon dioxide mixture in most inner cylindrical zone to be consumed in consecutive synthesis reactions or as fuel-oxidant in consecutive molten carbonate fuel cells, and with the emitted hot flue gas from the fuel cell and synthesis reactor to be used for at least partial heating of the far outer catalytic reaction zone by flowing it via the external surface of the far outer impermeable cylinder.

42. ^{1/30} (new) The process of claim 41, wherein the permeate hydrogen-carbon dioxide mixture from most inner membrane is used for methanol synthesis of gasoline range hydrocarbon synthesis in a consecutive chemical reaction step.

43. ^{1/31} (new) The process of claim 41 wherein the feed hydrocarbon is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, naphtha, gasoline, natural gas, coal gas rich in

methane, landfill gas rich in methane, flue gas rich in methane, biomass gas rich in methane.

1132
44.

(new) The process of claim 41 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH₄ and CO₂ mixture, acidic natural gas rich in CH₄ and CO₂, coal gas rich in CH₄ and CO₂, landfill gas rich in CH₄ and CO₂, biomass gas rich in CH₄ and CO₂, other primary, secondary, refinery, and flue gas mixtures rich in CH₄ and CO₂.

1133
45.

(new) The process of claim 41 wherein the inorganic or composite membrane of next inner permeable cylinder is rendered catalytic with the metal catalyst selected from the group consisting of nickel (Ni), chromium (Cr), ruthenium (Ru), rhodium (Rh), platinum (Pt), palladium (Pd), copper (Cu), zinc (Zn), cobalt (Co).